Spectroscopic properties of BN layers

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Abstract

Hexagonal boron nitride (h-BN) is a wide band gap semiconductor (~ 6.5 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering [1]. For instance electron mobility of graphene has been shown to be preserved when graphene is supported by a h-BN film.

Until recently, properties of h-BN materials were poorly known due to both the scarcity of crystals and suitable investigation tools. This situation has changed thanks, first, to the development of dedicated photoluminescence (PL) and cathodoluminescence (CL) experiments running at 4K and adapted to the detection in the far UV range [2, 3, 4], and second to the avaibility of high quality single crystals [5]. Thanks to these tools, h-BN has been shown to display original optical properties, governed, in the energy range 5.5 – 6 eV, by strong excitonic effects [2, 3, 6], in agreement with the most reliable theoretical calculations [7, 8]. Furthermore, experimental investigations combining cathodo-luminescence measurements and transmission electron microscopy (TEM) observations have revealed that excitonic luminescence is highly sensitive to their environment and are easily perturbed by structural defects such as dislocations [4].

In this talk, we will examine the interplay between structure, defects and spectroscopic properties of BN layers and how these properties can be further exploited for the characterization of these nanostructures. We carry out optical and structural characterizations of this material by combining PL, CL measurements at 4K in the UV range (up to 7eV), HRTEM observations and Electron Energy Loss Spectroscopy (EELS) in TEM and STEM modes. Thin layers have been obtained by mechanically exfoliating small crystallites or synthesized by CVD techniques. Exfoliated flakes were reported first on SiO_2 substrates for AFM thickness measurements, as described in [9] and second on TEM grids. CVD made layers were transferred on gold TEM grids.

We will show first, that, whatever the structure, bulk or nanoscale, excitonic luminescence consists of two series of lines called S and D. S excitons are found to be self-trapped, due to a Jahn-Teller effect [3]. Thanks to the imaging capability of the CL, emission, related to D lines, is found to be localized on defects, identified by TEM as grain boundaries (Figure 1). In defect free areas of thin layers, D lines completely vanish and S lines only are observed. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the layers [10].

Second, we will show that EELS provides an alternative approach to the nature of electronic excitations by inspecting the low losses in the 0 – 20 eV range. Pioneering work performed on BN SWNT has shown the potentialities of this approach [11]. One can indeed access under controlled illumination conditions, to the onset of optical transitions. Progress made recently in TEM instrumentation makes now possible the investigation of these transitions at a nm scale and with an energy resolution below 100 meV. We will discuss how these possibilities can be exploited for comparing structural properties of different BN layers.

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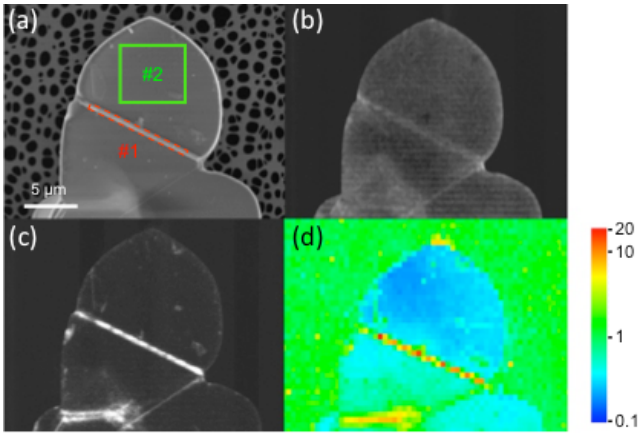

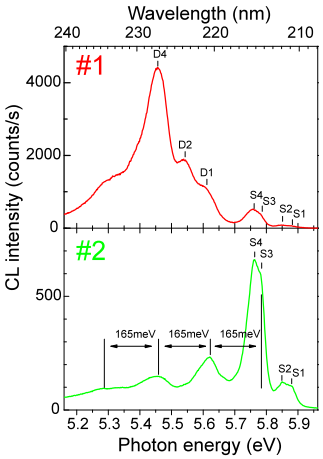

Figure: Left: a) MEB image of BN crystallite, b) and c) CL images recorded at the energy of the D4 and S3-S4 lines respectively, d) D/S ratio mapping. Right: CL spectra recorded in the areas labeled #1 (top) and #2 of the crystallite (bottom). Area #1 is a grain boundary.